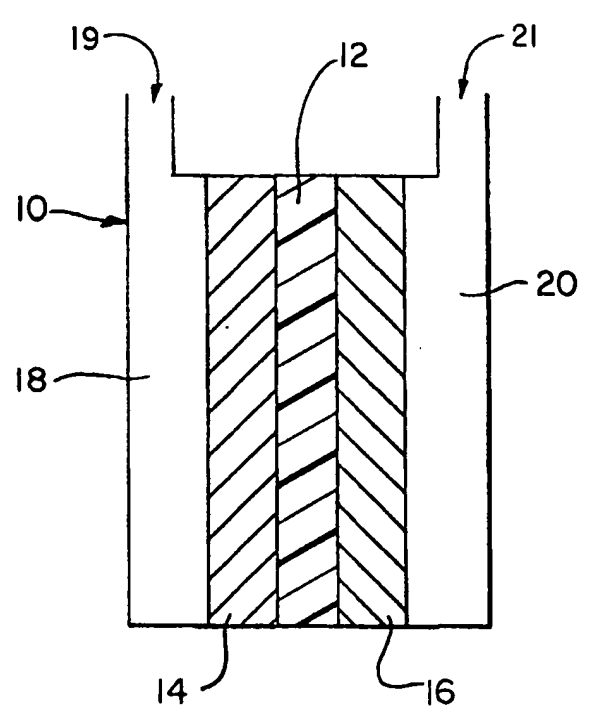




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US94/01427 <b>(22) International Filing Date:</b> 9 February 1994 (09.02.94) <b>(30) Priority Data:</b> 08/045,968 9 April 1993 (09.04.93) US <b>(71) Applicant:</b> MAXDEM INCORPORATED [US/US]; 140 East Arrow Highway, San Dimas, CA 91773 (US). <b>(72) Inventors:</b> OGATO, Naoya; 6-29-6, Asagaya-Kita, Suginami-ku, Tokyo 166 (JP). RIKUKAWA, Masahiro; Casa M-105, 3-17-4, Akatsukashin-machi, Itabashi-ku, Tokyo 175 (JP). <b>(74) Agents:</b> CHRISTIE, William, P. et al.; Christie, Parker & Hale, P.O. Box 7068, Pasadena, CA 91009-7068 (US).		<b>(81) Designated States:</b> CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> SULFONATED POLYMERS FOR SOLID POLYMER ELECTROLYTES  <b>(57) Abstract</b> <p>Sulfonated polyphenylene solid polymer electrolytes having high proton conductivity are provided, which are stable and which maintain high conductivity at temperatures of 100 °C and above. These membranes are useful as solid polymer electrolytes (12) in fuel cells (10) and can be operated above the boiling point of water.</p> 		

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**SULFONATED POLYMERS  
FOR SOLID POLYMER ELECTROLYTES**

Field of the Invention

This invention relates to stable sulfonated polyphenylene solid polymer electrolytes which have high proton conductivity characteristics. The sulfonated polyphenylene electrolytes are particularly useful in battery and fuel cell applications.

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Background of the Invention

Solid polymer electrolytes, SPE's, are ionic polymers having very high ion conductivity. As electrolytes they are useful in electrochemical systems, primarily in batteries and fuel cells. The polymeric nature of SPE's makes them much easier to handle than liquid electrolytes. The physical construction of the electrochemical cell is greatly simplified with the use of SPE's since elaborate seals and containment systems are not needed to contain corrosive liquid electrolytes. The use of SPE's in fuel cells and batteries is well established in the art.

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The use of solid polymer electrolytes can greatly simplify cell design. Liquid electrolytes must be confined with a separator and contained with seals. Liquid electrolytes are highly corrosive and more readily contaminated than solid electrolytes. Fuel and oxygen will diffuse across liquid electrolytes more readily, lowering efficiency. SPE's avoid these problems and can be made thinner, thereby lowering cell resistance.

1 Handling of SPE's is much easier than handling liquid systems, and cell construction can be simpler.

5 Fuel cells with SPE's promise greater energy density than liquid electrolyte cells because of low overall weight, primarily due to simpler construction and thinner cells. The first fuel cells flown in the U.S. space program used sulfonated polystyrene SPE's, and SPE cells are still a choice for space missions. (Alkaline cells are also used.)

10 An SPE should have the following properties:  
(1) high ionic conductivity, (2) zero electronic conductivity, (3) very low permeability to gases, (4) chemical stability at the operating temperature, (5) mechanical strength, (6) low sensitivity to humidity, 15 and (7) compatibility with catalyst.

The first of these is by far the most difficult to obtain. Current SPE's must be operated at temperatures and pressures where water is a liquid; otherwise, the membrane dehydrates, and proton conductivity is 20 drastically reduced. Although byproduct water must be removed, care must be taken not to dry out the SPE. Water management is a major difficulty of currently available SPE's. Fuel and air streams must be pre-humidified, and temperature strictly limited to avoid dehydration. These 25 extra control systems add significant weight and cost.

It would be highly advantageous to operate SPE fuel cells above the boiling point of water. This would greatly simplify water balance. Temperatures lower than about 80°C require active cooling with concomitant weight and cost. The key lies in development of an SPE with high 30 proton conductivity in the absence of condensed water. The need for hydration with sulfonated polyfluorocarbon SPE's is a result of the relatively low concentration of sulfonate groups and the hydrophobic nature of the fluorocarbon backbone. The structure of 35 perfluorosulfonated polymer membranes is such that the sulfonate groups tend to concentrate in a water rich

1 phase, which forms a network permeating the hydrophobic  
fluorocarbon regions. When dehydrated, the sulfonate  
groups become isolated, and proton migration between  
groups is difficult.

5 There is therefore a need for SPE's which maintain  
high proton conductivity above the boiling point of water  
and in the absence of liquid water.

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1     Summary of the Invention

          In accordance with practice of the present invention,  
a solid polymer electrolyte is provided which comprises a  
rigid-rod polyphenylene polymer which has been sulfonated  
5     to contain from about 1% to about 30% by weight sulfur.

          Products incorporating the rigid-rod polyphenylene  
polymer are also provided. In one embodiment, a fuel cell  
is provided which includes an anode and a cathode, along  
with means for introduction of fuel to the anode and means  
10    for introduction of oxidant to the cathode. The  
sulfonated polyphenylene polymer electrolyte of the  
present invention provides electrolytic contact between  
the anode and cathode.

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1     Brief Description of the Drawings

5         These and other features, aspects, and advantages of the present invention will be more fully understood when considered with respect to the following detailed description, appended claims, and accompanying drawings, wherein:

10         FIG. 1 is an elevation view of a sheet of film formed from a sulfonated rigid-rod polyphenylene polymer provided in accordance with practice of the present invention;

       FIG. 2 is a schematic view, in partial cross-section, of a fuel cell incorporating a sulfonated rigid-rod polyphenylene polymer electrolyte provided in accordance with practice of the present invention;

15         FIG. 3 is a graph of sulfonation level in mol percent as a function of reaction time (hrs) at room temperature provided by the Example 2 experiment; and

20         FIG. 4 is a graph showing the conductivity of sulfonated polymers having two different degrees of sulfonation.

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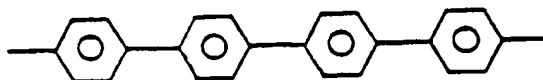




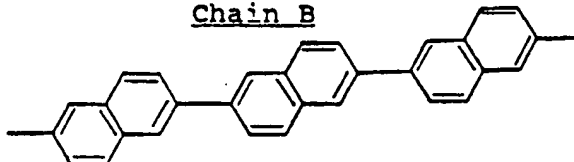
1 general structures shown here, for simplicity. All  
structures shown represent polymers with various extents  
of 1,4 linkages. Other linkages, including 1,2 phenylene  
linkages, 1,3 phenylene linkages, and all the possible  
5 naphthalene and anthracene linkages, are not shown, but  
implied.

The rigid-rod polymers of the present invention are  
linear polymers with parallel covalent bonds between the  
monomer units. The monomer units are not necessarily in  
10 a straight line. In some polymers, the majority of  
monomer units will be in a straight line (see chain A  
below). In other polymers, the monomer units will be  
staggered in a stair-like or crankshaft-like fashion (see  
chain B below). (The chain A and B monomer units are  
15 shown schematically without pendant organic side groups.)  
The monomer units can rotate about the linear axis of the  
covalent bonds between the monomers. However, the monomer  
units are restricted from flexing with respect to the  
bond, thus forming a rigid-rod polymer. Although the  
20 covalent bonds between the monomer units do not  
necessarily line up in a straight line, i.e., they may not  
be co-linear, the bonds are parallel, to yield a  
substantially linear rigid-rod polymer.

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Chain A

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Chain B

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1           Each phenylene unit may be substituted with groups  
R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> (collectively, R). Phenylene units may  
have all R's equal to H; that is, no side groups other  
than hydrogen. The number and type of R's are chosen to  
5 retain solubility of the polymer and to adjust other  
properties, such as reactivity to sulfonation.  
Preferably, at least 50% of the phenylene monomer units  
will have at least one non-hydrogen solubilizing side  
group R. More preferably, at least 80% of the phenylene  
10 monomer units will have a solubilizing side group.

The solubilizing side groups R may be chosen from a  
wide variety of functional groups, including but not  
limited to alcohol, aldehyde, alkaryl, alkoxy, alkyl,  
alkyl or aryl amide, alkyl ketone, alkyl sulfide,  
15 alkylsulfonate, alkylsulfonic acid, amide, amine,  
aralkyl, aryl, aryl ester, aryether,  
aryletheretherketone, aryetherketone, arylketone,  
aryloxy benzoyl, aryloxy, arylsulfide, arylsulfonate,  
arylsulfone, arylsulfonic acid, arylsulfoxide, benzoyl,  
20 carboxylic acid, ester, fluoro or polyfluoro alkyl,  
fluoro or polyfluoro aryl, heteroaryl, imide, imine,  
ketone, naphthyl, naphthoyl, phenoxybenzoyl, phenyl,  
sulfonamide, sulfonate, sulfone, sulfonic acid, -CHOHAr,  
-CHOHAr'-O-Ar, -CO<sub>2</sub>Ar, -CO-Ar'-O-Ar, -OCOAr, and the  
25 like, where -Ar is an aryl group and -Ar'- is an arylene  
group. A given rigid-rod composition may have two or more  
different R groups. The R groups may also be oligomeric  
or polymeric, for example, but not limited to  
poly(phenylene oxide), poly(ether ketone), poly(ether  
30 ether ketone), poly(phenylene sulfide), poly(ethylene  
oxide), and the like.

Rigid-rod polyphenylene polymers and the production  
thereof are disclosed in International Publication No.  
WO91/02764, and in corresponding U.S. patent application  
35 Serial No. 07/397,732, filed August 23, 1989 and allowed  
December 23, 1992. Publication No. WO91/02764 and

1 application No. 07/397,732 are fully incorporated herein  
by this reference.

5 The term "solubilizing group" means a functional  
group which, when attached as a side chain to the polymer  
in question, will render it soluble in an appropriate  
solvent system. It is understood that various factors  
must be considered in choosing a solubilizing group for a  
particular polymer and solvent, and that, all else being  
the same, a larger or higher molecular weight solubilizing  
10 group will induce a higher degree of solubility.  
Conversely, for smaller solubilizing groups, matching the  
properties of the solvent and solubilizing groups is more  
critical, and it may be more necessary to have, in  
addition, other favorable interactions inherent in the  
15 structure of the polymer to aid in solubilization.

One can estimate the compatibility of a solvent and  
pendant organic substituent type by comparing properties,  
such as dielectric constant and dipole moments. There are  
also various types of semi-empirical sets of parameters  
20 for non-polymeric materials (such as Hildebrand's  
solubility parameters - J.H. Hildebrand and R.I. Scott,  
The Solubility of Non-electrolytes, 3rd Ed., Dover  
Publications, NY, 1964 - and derivatives thereof) that can  
be used to estimate compatibility. Different sets of  
25 these solubility parameters have been developed to account  
for various types of solvent/solute interactions (e.g.,  
dispersion interactions, induction, and dipole  
interactions), and higher solubility is achieved as more  
of these sets of parameters are matched. Other factors  
30 being equal, a relatively higher molecular weight pendant  
organic group will have a greater effect than a relatively  
lower molecular weight group on the solubility  
characteristics of the overall polymer. Therefore, it is  
generally preferred that the solubilizing organic groups  
35 be of moderately high molecular weight; that is, molecular  
weight of greater than about 300. Furthermore, when the  
molecular weight of the pendant organic groups is greater

1       than about 300, they can act as the functional equivalent  
of the coil-like matrix of a molecular composite. Solubility can be provided, however, with pendant groups  
having very low molecular weight, such as phenyl groups,  
5       phenyl ketone groups, hydroxy groups, and the like.

Processes for preparing unsubstituted or alkyl substituted polyphenylenes from aryl Grignard reagents are described in T. Yamamoto et al, Bull. Chem. Soc. Jpn., 1978, 51, 2091 and M. Rehahn et al, Polymer, 1989, 30, 1054. Paraphenylene polymers (made up of monomer units of  
10       Formula IA) can be prepared by the coupling of Grignard reagents with paraphenyl dihalides catalyzed by transition metal complexes. Thus, a mixture of 4-bromophenylmagnesium bromide (1 mole) and 4-bromo-3-alkylphenylmagnesium bromide (0.01 mole), the alkyl group  
15       having an average chain length of about 24 carbon atoms, will react in an ether solvent in the presence of a transition metal complex to yield a polyparaphenylene rigid-rod polymer having about one monomer unit per 100  
20       monomer units substituted with a long-chain alkyl group. The transition metal-catalyzed coupling reaction proceeds selectively and quantitatively under mild conditions. In another variant of the reaction, 1,4-dibromobenzene (1.0 mole) and a 1,4-dibromobenzene substituted with a long-chain  
25       alkoxy group (0.1 mole) can be coupled in the presence of magnesium metal and a transition metal catalyst in an inert solvent, such as ether, to produce a polyparaphenylene rigid-rod polymer having, on the average, about one monomer unit out of 10 monomer units  
30       substituted with a long-chain alkoxy group. The net reaction resembles the dehalogenation polymerization of dihaloaromatic compounds with copper and sodium. Dibromosubstituted compounds are the compounds of choice for the reaction; however, in many instances, the dichloro  
35       compound can also be used if the reaction can be initiated. We have found that the  $\text{NiCl}_2$  (2,2'-bipyridine)

1 transition metal catalyst works satisfactorily for this reaction.

Coupling of the paradihaloarene monomers is preferably carried out with nickel or palladium catalysts, with zinc as the reducing agent. Such polymerizations give soluble rigid-rod polyparaphenylene polymers with high molecular weights in virtually quantitative yields. This approach has distinct advantages, since a wider variety of solvents can be employed, such as N,N-dimethylformamide (DMF), N-methylpyrrolidinone (NMP), hexamethylphosphoric triamide (HMPA), and benzene. This coupling reaction can also be used with monomers having specially reactive groups, such as nitrile and carbonyl groups. In addition, zinc is less expensive and easier to handle than magnesium.

It is highly recommended to utilize highly purified (preferably greater than about 99% pure) paradihalobenzene monomer from which any water or other aprotic impurities have been removed. For instance, a mixture of one equivalent of anhydrous nickel chloride, three equivalents of sodium iodide, seven equivalents of triphenyl phosphine, and 50 equivalents of zinc metal is effective in the polymerization of about 30 equivalents of substituted paradichlorobenzene monomer. The polymerization reaction is preferably carried out at about 50°C but is effective from about 25°C to about 100°C. The ratio of equivalents of monomer to equivalents of nickel catalyst can vary over the range from about 10 to about 5000, and the ratio of equivalents of zinc to equivalents of monomer is at least 1.0. The ratio of equivalents of phosphine ligands and inorganic salt promoter to equivalents of nickel catalyst varies from about 1.0 to about 10 or more.

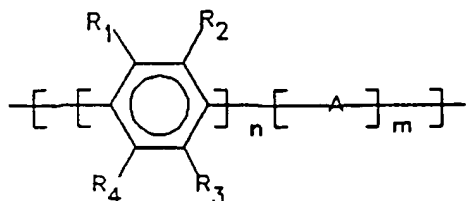
Aryl group coupling to afford polyphenylenes has also been effected by the palladium catalyzed condensation of haloaryl boronic acids as reported by Y. H. Kim et al, Polymer Preprints, 1988, 29, 310 and M. Rehahn et al,

1     Polymer, 1989, 30, 1060. The para-haloaryl boronic acid  
monomers required for formation of polyparaphenylenes can  
be prepared by the monolithiation of the paradihalobenzene  
5     with butyl lithium at low temperature and subsequent  
trimethylborate quench and aqueous acid workup. These  
polymerizations are carried out in aromatic and ethereal  
solvents in the presence of a base such as sodium  
carbonate. Therefore, this type of reaction is suitable  
10    for producing polyparaphenylenes substituted with organic  
groups such as alkyl, aryl, aralkyl, alkaryl,  
polyfluoroalkyl, alkoxy, polyfluoroalkoxy, and the like.

The monomer units are known or can be prepared by  
conventional chemical reactions from known starting  
15    materials. For example, the paradihalobenzene monomers  
substituted at the 2 position with an alkoxy group can be  
prepared from the corresponding 2,5-dihalophenol by  
allowing the phenol, in the presence of sodium hydroxide  
and benzyltriethylammonium chloride, to react with the  
20    corresponding 1-haloalkyl, such as 1-bromohexadecane.

In one embodiment of the present invention, the  
rigid-rod polyphenylene is a co-polymer. In another  
embodiment, it is a co-polymer of two or more rigid  
25    phenylene monomer units. In another embodiment, it is a  
co-polymer of at least one rigid phenylene monomer unit  
and at least one flexible monomer unit. The co-polymers  
may be random, block, graft, or other types known in the  
art. Preferably, the rigid-rod segments will have number  
30    average degree of polymerization of about 6 or greater.  
The following structure is a block co-polymer where -A-  
represents a flexible group, segment or block:

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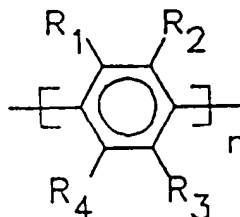


II

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wherein

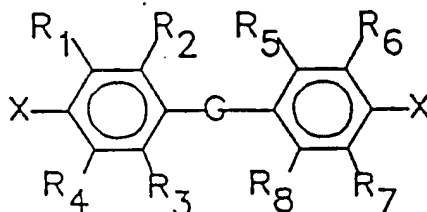
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is a rigid-rod polymer segment, wherein each  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  on each monomer unit, independently, is H or a solubilizing side group,  $n$  and  $m$  are 1 or greater, and  $-[A]-$  is a non-rigid segment, for example, as derived from non-rigid monomers of Structure III:

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III

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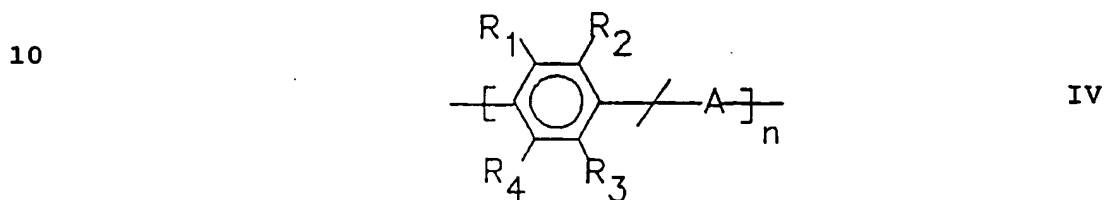
where  $R_1$ - $R_8$  are independently chosen from solubilizing side groups and H, wherein  $G$  is  $-O-$ ,  $-S-$ ,  $-CH_2-$ ,  $-CY_2-$ ,  $-OCH_2-$ ,  $-OAr-$ ,  $-O(ArO)_n-$ ,  $-(CH_2)_n-$ ,  $-(CY_2)_n-$ ,  $-CO-$ ,  $-CO_2-$ ,  $-CONY-$ ,  $-O(CH_2CH_2O)_n-$ ,  $-(CF_2)_n-$ ,  $-COArCO-$ ,  $-CO(CH_2)_nCO-$ ,  $-C(CF_3)_2-$ ,  $-C(CF_3)(Y)-$ ,  $-NY-$ ,  $-P(=O)Y-$ ,  $X$  is Cl, or Br, or I, and Ar is an aromatic group, heteroaromatic group, or substituted aromatic group, and  $Y$  is independently selected from the

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1 group consisting of H, F, CF<sub>3</sub>, alkyl, aryl, heteroaryl, or  
aralkyl group, and n is 1 or greater.

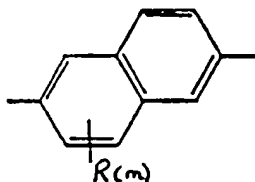
The following Structure IV shows a random co-polymer  
provided in accordance with the present invention  
5 comprising of a rigid-rod phenylene of Structure I and a  
flexible monomer unit -A-:



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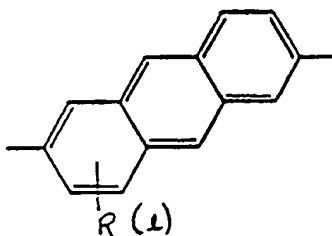
In another embodiment of the present invention the  
rigid-rod polyphenylene will comprise rigid naphthalene or  
anthracene monomer units, as follows:

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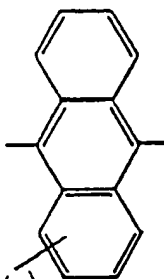
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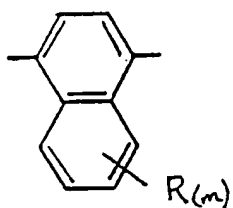
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VII

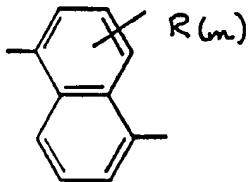
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VIII

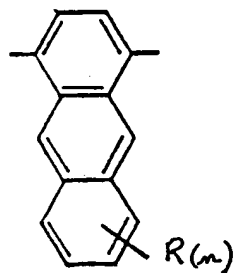
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IX

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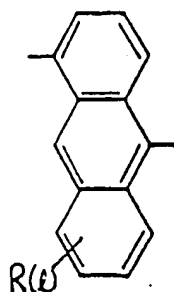


X

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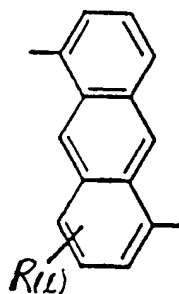
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XI

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XII

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wherein  $R_m$  and  $R_l$  are R groups as defined above, with  $m = 1$  to 6 and  $l = 1$  to 8.

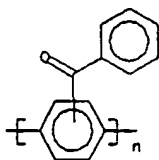
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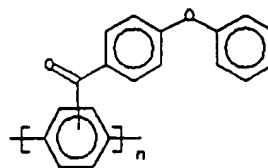
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Any position of the naphthalene or anthracene monomer units may bear solubilizing side groups. Non-rigid-rod monomer units may also be included, with preferably less than 20%, and more preferably less than 10% of the monomer units being non-rigid-rod units. Non-rigid-rod units are defined to include naphthalene units linked in the 1,3 or 1,6 or 2,7 positions, or anthracene units linked in the 1,3 or 2,7, or other non-parallel linkages of naphthalene or anthracene units. Flexible units, segments, blocks, or grafts -A- may also be included in the rigid-rod polyphenylenes having naphthalene or anthracene units.

1 With the polymers of the present invention  
incorporating phenylene units of the Structure I, if one  
of the R's is benzoyl, with the other R's being hydrogen,  
and most of the linkages are -1,4- phenylene linkages,  
5 polymer 1 poly(benzoyl-1,4-phenylene) results. If one of  
the R's is 4-phenoxybenzoyl, with the other R's being  
hydrogen, the rigid-rod polyphenylene is poly(4-  
phenoxybenzoyl-1,4-phenylene) 2.



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Note that the R groups benzoyl and 4-phenoxybenzoyl may be  
randomly distributed between the 2 and 3 positions of the  
phenylene units.

Because of their unusual structure rigid-rod  
polyphenylene polymers such as 1 and 2 have remarkable  
physical properties. They are the stiffest and hardest of  
all known isotropic thermoplastics. They have excellent  
chemical and thermal stability. And they are processable  
by both solution and thermal techniques.

Ionic groups can be introduced into polyphenylenes by  
sulfonation. Either the phenylene backbone or side groups  
or both may be sulfonated. The aromatic rings of both  
polymers 1 and 2 can be sulfonated using standard  
techniques. Exemplary, but non-limiting sulfonation  
methods include: treatment with concentrated sulfuric  
acid, treatment with fuming sulfuric acid, treatment with  
chlorosulfonic acid  $\text{ClSO}_3\text{H}$  followed by hydrolysis, or by  
treatment with a mixture of sulfuric acid and thionyl  
chloride. The time and temperature required will depend  
on the particular side groups of the polyphenylene being

1 sulfonated. In general, sulfonation conditions for a  
given rigid-rod polyphenylene can be determined as  
follows. The rigid-rod polyphenylene composition to be  
5 sulfonated (the test polymer) is first treated with  
concentrated sulfuric acid at room temperature for 16 hr  
and worked up as in Example 2 below. The resulting  
material is analyzed for sulfonic acid groups by  
titration. If the level of sulfonation is too low, the  
test sulfonation is repeated using more strenuous  
10 conditions roughly in the order:

	<u>Time</u>	<u>Temperature</u>	<u>Sulfonation Agent</u>
	24 hr	25°C	conc. sulfuric acid
	48 hr	25°C	"
	96 hr	25°C	"
15	200 hr	25°C	"
	24 hr	50°C	"
	24 hr	100°C	"
	48 hr	50°C	"
	24 hr	25°C	fuming sulfuric acid
	24 hr	50°C	"
	48 hr	50°C	"
20	24 hr	50°C	chlorosulfonic acid
	24 hr	100°C	"

The test sulfonation is repeated until the desired degree  
of sulfonation determined by titration is reached. In  
some cases sensitive side groups will not withstand  
25 sulfonation conditions and an alternate route involving  
protection of side groups or later incorporation of  
sensitive side groups will be necessary. Methods for  
protection and further elaboration of side groups will be  
apparent to those skilled in the art. The degree of  
30 sulfonation may be followed by other methods as  
convenient, including but not limited to elemental  
analysis, x-ray fluorescence, secondary electron or  
microprobe analysis.

If the initial test sulfonation conditions result in  
35 excessive sulfonation then the reaction temperature may be  
lowered or reaction time decreased to reach desired  
levels. In general, the mildest conditions which lead to

1 desired levels of sulfonation should be sought. For  
example, sulfonation of the polymer 2 in sulfuric acid at  
room temperature for 200 hr gives nearly the same level of  
sulfonation obtained after reaction for 400 hours. The  
5 phenoxy group of 2 polymer is relatively easily  
sulfonated. Films and membranes prepared from sulfonated  
polyphenylenes provided in accordance with the present  
invention, such as the polymers 1 and 2, have high proton  
conductivity.

10 The degree of sulfonation of the polyphenylene  
polymers of the present invention is preferably at least  
1% by weight, i.e., the weight of sulfur in the polymer  
divided by the total weight of the polymer is at least 1%.  
At levels less than 1%, the conductivity of the polymer is  
15 less than desired. While there is no upper limit to the  
preferable degree of sulfonation, it is not practical to  
provide a polymer where the percent by weight sulfur is  
greater than about 30%.

The degree of sulfonation may also be defined in  
20 terms of mole percent by converting the above-described  
weight percent to a mole percent value. For example, in  
polymer 2, the molecular weight of the monomer unit is  
272. Each sulfonic acid group adds a molecular weight of  
80 to the monomer unit. If each monomer unit is  
25 sulfonated once (on the average), the mole percent  
sulfonated is 100%. The molecular weight of the  
sulfonated monomer unit would be 352, and the percent  
sulfur by weight is  $32/352 = 9.1\%$ . If each monomer unit  
is sulfonated twice (on the average), the mole percent  
30 sulfonation is 200%, and the percent sulfur by weight is  
 $64/(272 + 2 \times 80) = 15\%$ .

While not wishing to be bound by theory the high  
conductivity of the rigid-rod SPE's results from the  
linear array of sulfonic acid groups along the backbone.  
35 Such arrangement facilitates transport of protons along  
the chain. The rigidity of the polymer backbone also  
prevents clustering of sulfonate groups and formation of

1 isolated regions of ionic groups which would prevent ion  
mobility.

5 Solid polymer electrolytes comprising sulfonated  
rigid-rod polyphenylene may be homopolymers, block co-  
polymers with rigid-rod blocks, random co-polymers,  
blends, alloys, mixtures, and the like. For the purposes  
of this invention rigid-rod polyphenylenes are taken to be  
10 polymers which incorporate sidechain substituted or  
unsubstituted rigid-rod polyphenylene blocks having number  
average block length of about six or more, or blocks of  
naphthalene or anthracene monomer units having rigid-rod  
or crankshaft structures and number average block lengths  
of about six or more.

15 While SPE's are typically used in the form of a  
membrane other structures may be possible. For example,  
referring to FIG. 1, a sheet or film 10 of a sulfonated  
rigid-rod polyphenylene provided in accordance with the  
present invention is shown. Such a film can be provided  
by various film-forming techniques, including extrusion,  
20 casting, and the like.

For fuel cell applications the SPE is typically in  
intimate physical contact with the electrodes, catalyst,  
current collector and other supporting structure. The SPE  
may not have readily distinguished physical boundaries.  
25 It may be used as part of a gas diffusion electrode where  
gas, liquid and solid form a complex interface. The  
methods of construction of such electrodes and cells are  
well known in the art. For example, turning to FIG. 2, a  
schematic illustration of a fuel cell 11 incorporating a  
30 solid polymer electrolyte comprising a sulfonated rigid-  
rod polyphenylene 12 provided in accordance with practice  
of the present invention is provided. The sulfonated  
polyphenylene separates and provides electrolytic contact  
between the anode 14 and the cathode 16. Fuel is  
35 introduced into the compartment 18 via the inlet 19 for  
contact with the anode 14, while oxidant is introduced

1       into the compartment 20 via the inlet 21 for contact with  
the cathode 16.

          The sulfonated polyphenylenes of the present  
invention will have other applications besides fuel cells.  
5       For example, the SPE's of the present invention will be  
useful as battery separators, electrolytes for  
electrosynthesis cells, electrolytes for electrolysis  
cells, electrolytes for gas generating electrochemical  
systems, as ionic membranes in electrochemical sensors, as  
10       electrolytes in electrochemical scrubbers and other  
purification systems, and as electrolytes in primary and  
secondary batteries. In some of these applications the  
SPE will be used in a salt form, for example with sodium  
counter ions or other alkali metal cation counter ions.  
15       Other applications for the SPE's of the present invention  
will be apparent to one skilled in the art.

          It will be understood by one skilled in the art that  
the exact composition of the SPE will depend on its  
environment. The degree of hydration will depend on the  
20       humidity and temperature. If the SPE is immersed in a  
liquid the composition of the liquid will determine the  
state of the SPE. The SPE may exchange protons, other  
cations, and to some extent anions with the surrounding  
solution. The pH of the SPE may be changed by adjusting  
25       the pH of the liquid phase in contact with the SPE. The  
SPE may be entirely in the acid form, meaning essentially  
all of the sulfonic groups are protonated. The SPE may be  
in the sodium form where all the sulfonic groups have  
sodium cations as counter ions. Other cations may be used  
30       such as cesium, potassium, lithium, calcium, magnesium,  
quaternary amines, or combinations of these. Transition  
metals and heavy metals may also be counter ions, for  
example where the ionic membrane is used to separate  
mixtures of metal salts.

35       It will also be apparent to one skilled in the art  
that the ionic polymers comprising the SPE's of the  
present invention may be crosslinked to various extents.

1 Crosslinking changes the solubility and mechanical  
properties of the SPE. Lightly crosslinked materials will  
swell greatly in compatible solvents; more highly  
crosslinked polymers will swell less. Crosslink density  
5 may be used to optimize the ionic conductivity by  
controlling the amount of solvent absorption into the SPE  
network. Crosslinks may be formed before, during, or  
after sulfonation. Typically, a bifunctional reactive  
compound is mixed and allowed to react with the ionic  
10 polymer.

#### GENERAL PROCEDURES

##### 1. 2,5-dichlorobenzoyl-containing Compounds

A wide variety of 2,5-dichlorobenzoyl-containing  
compounds (e.g., 2,5-dichlorobenzophenones and 2,5-  
15 dichlorobenzamides) can be readily prepared from 2,5-  
dichlorobenzoylchloride. Pure 2,5-dichlorobenzoylchloride  
is obtained by vacuum distillation of the mixture obtained  
from the reaction of commercially available 2,5-  
dichlorobenzoic acid with a slight excess of thionyl  
20 chloride in refluxing toluene. 2,5-dichlorobenzophenones  
(e.g., 2,5-dichlorobenzophenone, 2,5-dichloro-4'-  
methylbenzophenone, 2,5-dichloro-4'-methoxybenzophenone,  
and 2,5-dichloro-4'-phenoxybenzophenone) are prepared by  
the Friedel-Crafts benzoylations of an excess of benzene  
25 or substituted benzenes (e.g., toluene, anisole, or  
diphenyl ether, respectively) with 2,5-  
dichlorobenzoylchloride at 0-5°C using 2-3 mole  
equivalents of aluminum chloride as a catalyst. The solid  
products obtained upon quenching with water are purified  
30 by recrystallization from toluene/hexanes. 2,5-  
dichlorobenzoylmorpholine and 2,5-dichloro-  
benzoylpiperidine are prepared from the reaction of 2,5-  
dichlorobenzoylchloride and either morpholine or  
piperidine, respectively, in toluene with pyridine added  
35 to trap the hydrogen chloride that is evolved. After  
washing away the pyridinium salt and any excess amine, the  
product is crystallized from the toluene solution.



1            2.    Activated Zinc Powder

          Activated zinc powder is obtained after 2-3 washings  
of commercially available 325mesh zinc dust with 1 molar  
hydrogen chloride in diethyl ether (anhydrous) and drying  
5    *in vacuo* or under inert atmosphere for several hours at  
about 100-120°C. The resulting powder should be sifted  
(e.g., a 150mesh sieve seems to be satisfactory), to  
remove the larger clumps that sometimes form, to assure  
high activity. This material should be used immediately  
10    or stored under an inert atmosphere away from oxygen and  
moisture.

Example 1

Preparation of Poly(Benzoyl-1,4-phenylene)

15            Anhydrous bis(triphenylphosphine) nickel(II) chloride  
(34.7g; 53mmole), triphenylphosphine (166.6g; 741mmole),  
sodium iodide (34.6g, 231mmole), and 325mesh activated  
zinc powder (181.8g, 2.8mole) are weighed into a bottle  
under an inert atmosphere and added to an oven dried 12-  
20    liter flash containing 1.6 liters of anhydrous N-  
methylpyrrolidinone (NMP), against a vigorous nitrogen  
counterflow. This mixture is stirred for about 15  
minutes, leading to a deep red coloration. Solid 2,5-  
dichlorobenzophenone and another 0.8 liters of anhydrous  
25    NMP are then added to the flask. After an initial slight  
endotherm (due to dissolution of monomer), the temperature  
of the vigorously stirred reaction mixture warms to about  
60°C over 30 minutes and is held there (60-65°C) by use of  
a cooling bath. After stirring for an additional 10-15  
30    minutes, the viscosity of the reaction mixture increases  
drastically, and stirring is stopped. After heating this  
mixture for several days at 65°C, the resulting viscous  
solution is poured into 10L of 1 molar hydrochloric acid  
in ethanol to dissolve the excess zinc metal and to  
35    precipitate the macromonomer. This suspension is filtered  
and the precipitate triturated with acetone and dried to  
afford 283g (85% yield) of a fine pale yellow powder.

1

Example 2Preparation of Poly(4-phenoxybenzoyl-1,4-phenylene)  
2,5-Dichloro-4'-phenoxybenzophenone

5 To a 22L open-mouth round bottom flask fitted with a  
three-necked flange head, a mechanical stirrer, a nitrogen  
inlet and an outlet connected to a HCl scrubbing tower, is  
added 2,5-dichlorobenzoic chloride (4500g, 21.5mol) and  
phenyl ether (5489g, 32.3mol). The solution is cooled in  
10 ice to 5°C under stirring, and aluminum chloride (3700g,  
27.8mol) is added slowly, over a period of about 10  
minutes. The temperature of the reaction mixture is about  
35°C after the addition. The mixture is then stirred for  
about 30 minutes and poured into about 20 gallons of ice  
water. The large reddish mass is dissolved by adding  
15 about 12L of methylene chloride and stirring. The organic  
layer is separated and the aqueous layer is extracted with  
some methylene chloride. After methylene chloride is  
removed from the combined organic layer by distillation,  
the residue is recrystallized twice from cyclohexane  
20 (2x10L), washed with cooled hexane, air dried, and then  
vacuum dried, to afford 5387g monomer (73%). The mother  
liquor is kept for later recovery of remaining product.

Poly(4-phenoxybenzoyl-1,4-phenylene)

25 To a 12L open-mouth round bottom flask equipped with  
a flange head, an air driven stirrer, a thermowell with a  
thermocouple, and a nitrogen purge line, is added under  
nitrogen bis(triphenylphosphine)nickel(II) chloride  
(58.2g, 88.9mmol), sodium iodide (54.7g, 365mmol),  
30 triphenylphosphine (279.3g, 1065mmol), 325mesh activated  
zinc dust (239.5g, 3663mmol) and anhydrous  
N-methylpyrrolidinone (NMP) (3400ml). The solution is  
stirred and heated with a hot air gun to 40°C. The  
monomer 2,5-dichloro-4'-phenoxybenzophenone (935g,  
35 2725mmol) is added. After about 15 minutes, the mixture  
becomes viscous. After 17 minutes, the solution becomes

1 very thick, and the stirring is stopped. The reaction  
mixture is allowed to come to room temperature and is left  
to stand overnight. The next morning, the reaction  
mixture is coagulated into an acetone bath and ground up  
5 in a blender. The crude polymer is then stirred for  
several days in 1 molar hydrochloric acid in ethanol to  
remove the excess zinc metal. The polymer is collected by  
filtration, washed with water and acetone, and dissolved  
in 16L of methylene chloride. The solution is filtered  
10 through 10 $\mu$ m polypropylene membrane with the aid of  
celite, coagulated in the same volume of acetone,  
filtered, extracted with acetone for three days, and  
dried, to afford 700g pale yellow polymer (94%).

15

### Example 3

#### Sulfonation of Poly(4-phenoxybenzoyl-1,4-phenylene)

Twenty five grams of poly(4-phenoxybenzoyl-1,4-phenylene), provided in accordance with a process such as that outlined in Example 2, was dissolved in chloroform  
20 and was reprecipitated by pouring into excess methanol. This process was repeated three times. The resulting solid was oven dried overnight at 100°C. The dry solid was pulverized by hand in a mortar and pestle. Ten grams of pulverized poly(4-phenoxybenzoyl-1,4-phenylene) was  
25 dissolved in 100ml concentrated sulfuric acid under a nitrogen atmosphere. The solution was held at room temperature for the desired time (see figure) and then poured into a large excess of water. The precipitate was collected by filtration and washed with water. The  
30 precipitate was pulverized and washed with water until the wash water came to pH = 7. The sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) was then dialyzed against distilled water using a cellulose acetate membrane.

35

The degree of sulfonation was determined by the following procedure. One gram of sulfonated polymer was placed in 1N aqueous sodium hydroxide, and the solution

1 was kept at room temperature for 1 day. The solution was  
then back titrated with 1N HCl using phenolphthalein as an  
indicator. FIG. 3 shows the level of sulfonation (mol%)  
relative to the reaction time at room temperature.

5

#### Example 4

##### Preparation of SPE Membranes with Sulfonated Poly(4-phenoxybenzoyl-1,4-phenylene)

A sulfonated polymer prepared in accordance with the  
10 procedure of Example 3 was dissolved in N-methyl-  
pyrrolidinone (NMP) and reprecipitated into  
tetrahydrofuran. The reprecipitated polymer was dried and  
redissolved in NMP to make a 2% by weight solution.  
Portions of this solution were cast onto clean glass  
15 plates and dried under a nitrogen stream at 100°C for 10  
hours. After drying, the membranes were removed from the  
glass support to give films with thicknesses between 10  
and 20 microns. These membranes were washed with methanol  
to remove the last traces of NMP and dried at 100°C under  
20 vacuum for 1 hour.

#### Example 5

##### Measurement of Proton Conductivity of Membranes of Sulfonated Poly(4-phenoxybenzoyl-1,4-phenylene)

25 Casting film samples (13mm in diameter, 10-20μm in  
thickness) of sulfonated poly(4-phenoxybenzoyl-1,4-  
phenylene) prepared in accordance with the procedure of  
Example 4 were kept under the saturated vapor pressure of  
water at room temperature in a desiccator for 1 week prior  
30 to the measurements. The first sample had a 65.8 mol%  
sulfonation, while the second sample was 80 mol%  
sulfonated. The wet casting film samples were sandwiched  
between platinum electrodes for electrical contacts and  
packed in a sealed cell with stainless steel terminals  
35 which were in contact with the measuring system.  
Conductivity of the film was measured with a Yokokawa-  
Hewlett-Packard Model 4192A LF impedance analyzer over the

1 frequency range 5 Hz to 13 MHz (OSC level 12 mV). The  
complex impedance method was used to determine  
conductivity.

5 The conductivity values as a function of temperature  
for two samples having different degrees of sulfonation  
are shown in FIG. 4. The conductivity peaks at about 0.02  
S/cm at about 80°C. At 110°C the conductivity for both  
samples is still above  $4 \times 10^{-3}$  S/cm.

10 The above descriptions of exemplary embodiments of  
sulfonated polymers provided in accordance with the  
present invention are for illustrative purposes. Because  
of variations which will be apparent to those skilled in  
the art, the present invention is not intended to be  
15 limited to the particular embodiments described above.  
The scope of the invention is described in the following  
claims.

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1 WHAT IS CLAIMED IS:

1. A solid polymer electrolyte comprising a rigid-rod polyphenylene which has been sulfonated to contain from 1% to 30% by weight sulfur.

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2. The solid polymer electrolyte of claim 1, wherein said rigid-rod polyphenylene has been sulfonated to 10% to 25% by weight sulfur.

10

3. The solid polymer electrolyte of claim 1, wherein the said sulfonated rigid-rod polyphenylene is part of a co-polymer.

15

4. The solid polymer electrolyte of claim 1, wherein the solubilizing groups R are selected from the groups consisting of -COAr, -CHOHAr, -OAr, -COAr'-O-Ar, alkaryl, alkyl, aralkyl, aryl, ester, and phenyl, where Ar is aryl and Ar' is arylene.

20

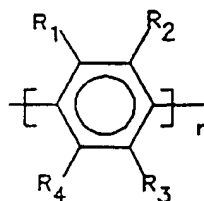
5. The solid polymer electrolyte of claim 1, wherein at least 80% of the phenylene units in the polyphenylene backbone are para or 1,4 linked.

25

6. The solid polymer electrolyte of claim 1, wherein at least 95% of the phenylene units in the polyphenylene backbone are para or 1,4 linked.

30

7. The solid polymer electrolyte of claim 1, wherein the said rigid-rod polyphenylene has the structure:



1        wherein  $R_1 - R_4$  are solubilizing groups or -H, and n is 6  
or greater, wherein the polymer has been sulfonated to  
contain from 1% to 50% by weight sulfur.

5            8. The solid polymer electrolyte of claim 7,  
wherein  $R_1$  is phenoxybenzoyl, and  $R_2 - R_4$  are H.

9. The solid polymer electrolyte of claim 7,  
wherein  $R_1$  is benzoyl, and  $R_2 - R_4$  are H.

10

10. The solid polymer electrolyte of claim 7,  
wherein  $R_1 = R_2 = R_3 = R_4 = H$  on 0% to 20% of the phenylene units.

11. A fuel cell comprising an anode, a cathode,  
15 means for introduction of fuel to the anode, means for  
introduction of oxidant to the cathode, and a solid  
polymer electrolyte of claim 1, providing electrolytic  
contact between said anode and cathode.

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## AMENDED CLAIMS

[received by the International Bureau on 17 May 1994 (17.05.94);  
original claims 1-11 replaced by amended claims 1-11 (2 pages)]

1

1. An ion exchange structure comprising a solid polymer electrolyte comprising a rigid-rod polyphenylene which has been sulfonated to contain from 1% to 30% by weight sulfur.

5

2. The ion exchange structure of claim 1, wherein the rigid-rod polyphenylene has been sulfonated to 10% to 25% by weight sulfur.

10

3. The ion exchange structure of claim 1, wherein the sulfonated rigid-rod polyphenylene is part of a copolymer.

15

4. The ion exchange structure of claim 1, wherein the rigid-rod polyphenylene polymer includes solubilizing pendant groups R selected from the groups consisting of -COAr, -CHOHAr, -OAr, -COAr'-O-Ar, alkaryl, alkyl, aralkyl, aryl, and ester, where Ar is

20

aryl and Ar' is arylene.

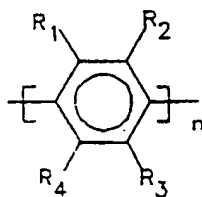
5. The ion exchange structure of claim 1, wherein at least 80% of the phenylene units in the polyphenylene backbone are 1,4 linked.

25

6. The ion exchange structure of claim 1, wherein at least 95% of the phenylene units in the polyphenylene backbone are 1,4 linked.

30

7. The ion exchange structure of claim 1, wherein the rigid-rod polyphenylene has the structure:



35



1 wherein  $R_1 - R_4$  are solubilizing groups or  $-H$ , and  $n$  is  
6 or greater.

8. The ion exchange structure of claim 7, wherein  
5  $R_1$  is phenoxybenzoyl, and  $R_2 - R_4$  are  $H$ .

9. The ion exchange structure of claim 7, wherein  
 $R_1$  is benzoyl, and  $R_2 - R_4$  are  $H$ .

10 10. The ion exchange structure of claim 7, wherein  
 $R_1 = R_2 = R_3 = R_4 = H$  on 0% to 20% of the phenylene units.

11. A fuel cell comprising an anode, a cathode,  
means for introduction of fuel to the anode, means for  
15 introduction of oxidant to the cathode, and a solid  
polymer electrolyte comprising a rigid-rod polyphenylene  
which has been sulfonated to contain from 1% to 30% by  
weight sulfur for providing electrolytic contact between  
the anode and cathode.

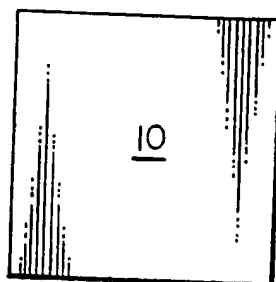
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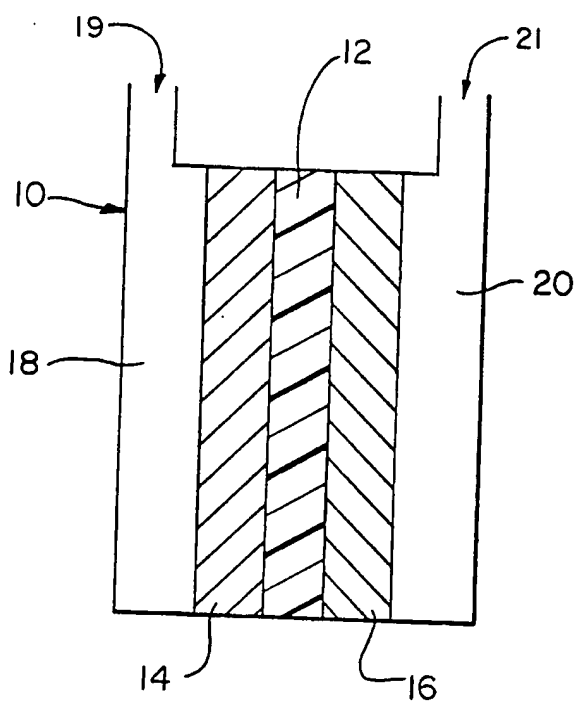
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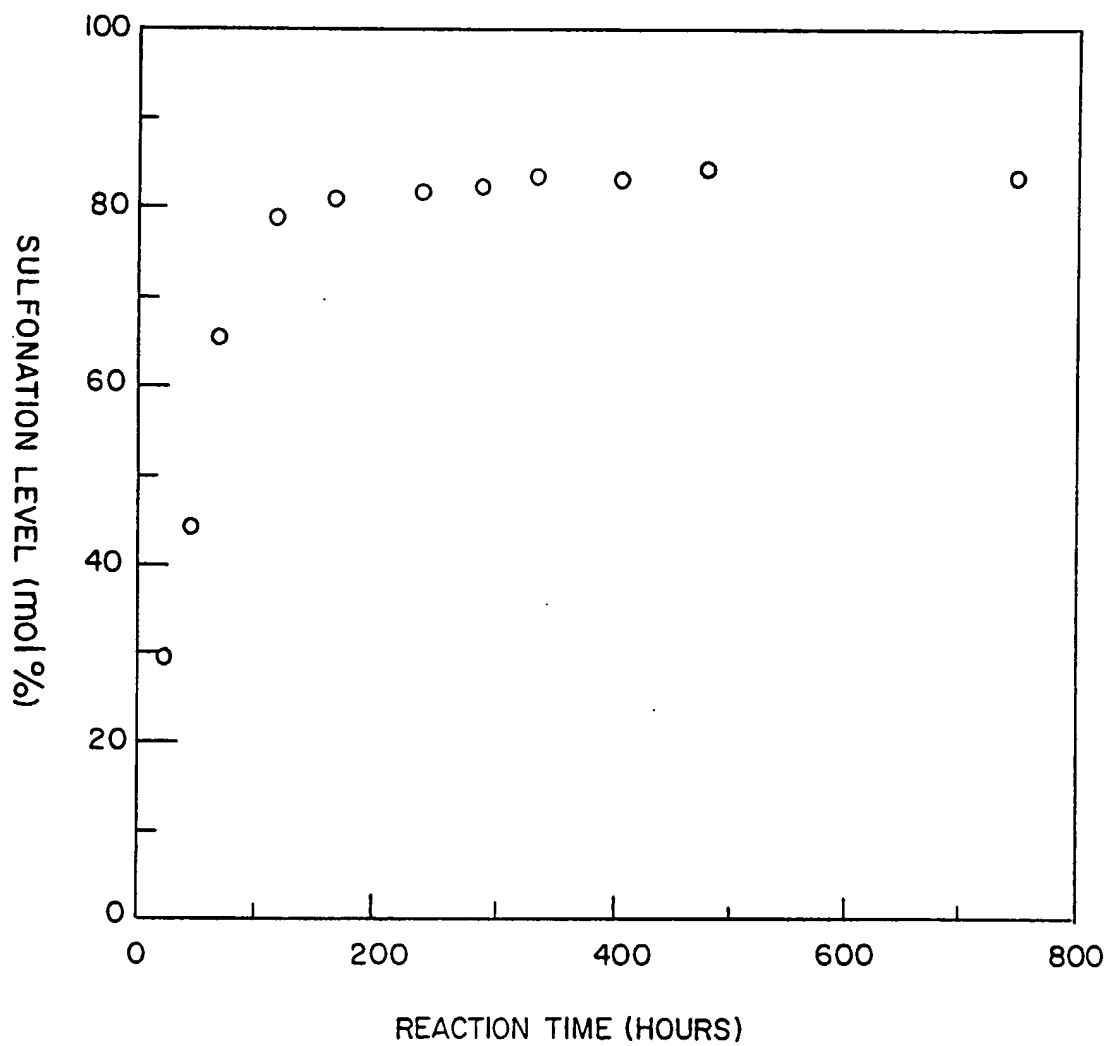
*Fig. 1*

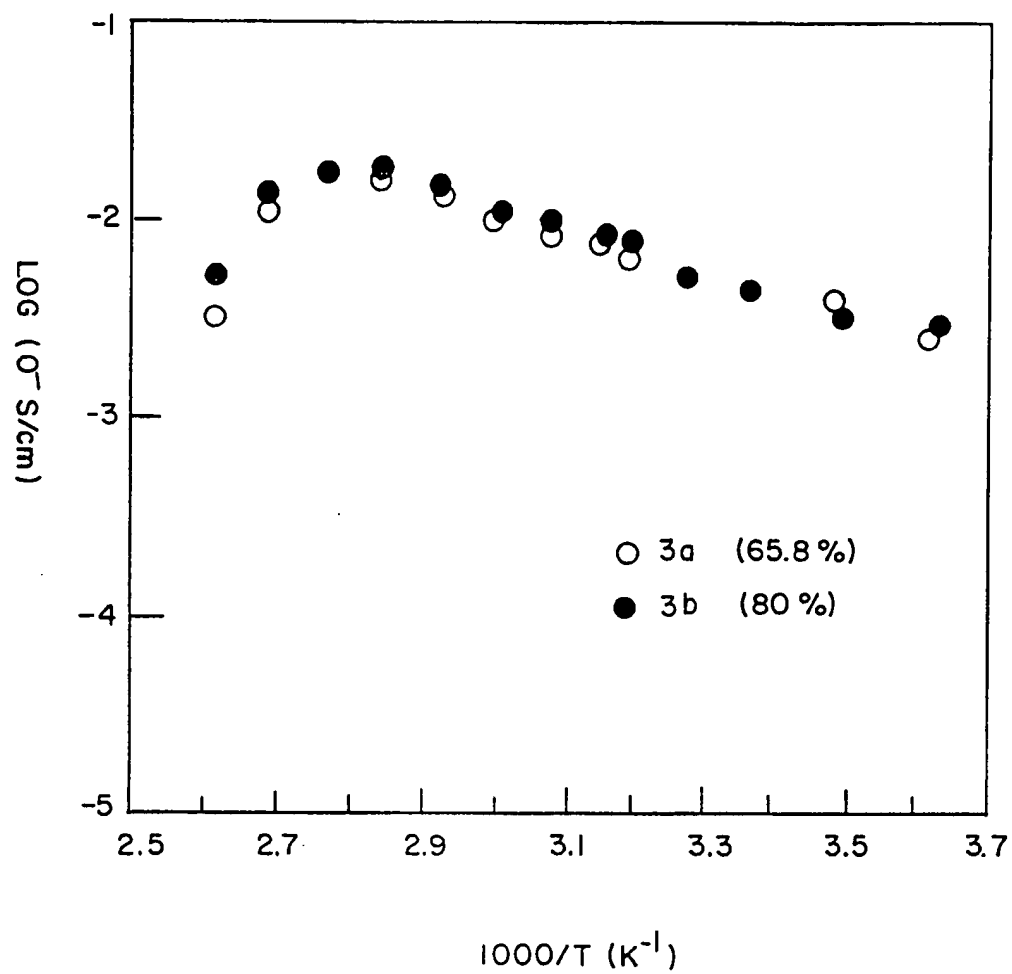


*Fig. 2*



2/3

*Fig. 3*

*Fig. 4*

## INTERNATIONAL SEARCH REPORT

International application No.

94/01427

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :H01M 8/10

US CL :429/33

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/33, 192; 252/62.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US, A, 5,227,457 (Marrocco et al.) 13 July 1993, col. 9, lines 11-14 and 67.	1-10
X	US, A, 3,484,293 (Hodgdon) 16 December 1969, col. 3, lines 49-75.	1-7, 10, 11
A	US, A, 4,943,499 (Casalbore-Miceli et al.) 24 July 1990, col. 1, lines 36-60.	1-11
A	US, A, 3,651,030 (Desaulniers et al.) 21 March 1972, col. 2, lines 10-68.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A document defining the general state of the art which is not considered to be of particular relevance	*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O document referring to an oral disclosure, use, exhibition or other means	
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Date of the actual completion of the international search

08 MARCH 1994

Date of mailing of the international search report

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